Draft Translation 696

January 1979

ON THE ORIGIN OF MINERAL
IMPURITIES IN ICE

E.E. Picciotto

UNITED STATES ARMY
CORPS OF ENGINEERS
COLD REGIONS RESEARCH AND ENGINEERING LABORATORY
HANOVER, NEW HAMPSHIRE, U.S.A.

CRREL

79 01 16 054

NOTICE

The contents of this publication have been translated as presented in
the original text. No attempt has been made to verify the accuracy of
any statement contained herein. This translation is published without
copy editing or graphics preparation in order to expedite the dissemina-
tion of information. Requests for additional copies of this document
should be addressed to the Defense Documentation Center, Cameron Station,
Alexandria, Virginia 22314.

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER Draft Translation 696	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) ON THE ORIGIN OF MINERAL IMPURITIES IN ICE (SUR L'ORIGINE DES IMPURETES MINERALES DE LA GLACE)		5. TYPE OF REPORT & PERIOD COVERED Translation
		6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s) E.E. Picciotto		8. CONTRACT OR GRANT NUMBER(s)
9. PERFORMING ORGANIZATION NAME AND ADDRESS		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS
11. CONTROLLING OFFICE NAME AND ADDRESS U.S. Army Cold Regions Research and Engineering Laboratory Hanover, New Hampshire		12. REPORT DATE January 1979
		13. NUMBER OF PAGES 24
14. MONITORING AGENCY NAME & ADDRESS(if different from Controlling Office) 25 P'		15. SECURITY CLASS. (of this report) Unclassified
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)

Approved for public release; distribution unlimited.

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

CRREL-TL-696

18. SUPPLEMENTARY NOTES

Translation by International Translation Co., West Peabody, Massachusetts.
CRREL Bibliography number 32-3814.

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

Glaciers
Ice
Impurities
Isotope impurities
Land ice

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

Mineral impurities can originate from four main sources: the ocean, the lithosphere, extra-terrestrial space and man's activities. Whatever the particular objective envisaged, besides analytical problems, any research in this field faces a common general problem: determination of the relative contributions from each source. This paper discusses chemical and isotopic methods which will give a solution to this problem. The main difficulty lies in the large chemical fractionations which appear to take place at all stages of the

DD FORM 1473 EDITION OF 1 NOV 65 IS OBSOLETE

037 100

Abstract (cont'd)

passage between the source and the place of deposition. Two cases of definite identification of the origin will be presented: evaluation of the extra-terrestrial component in firn samples from Plateau Station (East Antarctica) based on the measurement of ^{53}Mn, and the identification of a man-made component in the Pb found in an alpine glacier, based on the relative abundance of the stable isotopes of Pb.

TITLE: ON THE ORIGIN OF MINERAL IMPURITIES IN ICE

AUTHOR: E. E. Picciotto

SOURCE: Symposium on Isotopes and Impurities
         in Snow, Grenoble, 1975.
         IAHS-AISH Publication 118, p. 78-87.

GENERAL THEORY

/78/*   Other than a purely descriptive objective, consisting of list-

ing the chemical elements present in a specific geosphere, studies

on the chemistry of glaciers involve determining more general para-

meters, either in order to derive from them a current value, or to trace

their evolution in the past and from this to deduce information on

the history of the atmosphere, making use of the exceptional char-

acter of glaciers, polar glaciers in particular, i.e.: the ability

to record certain factors defining the state of the atmosphere and

maintaining these records faithfully over tens of thousands of years.

I have undertaken to treat briefly the following problem that is

encountered by those who study the chemistry of glaciers:

Given the contents of certain elements in snow, firn, or

ice samples, to determine the sources of these elements

and the relative contribution of each of these sources.

*Numbers in slashes in the left-hand margin indicate the original
French page.

I will adhere only to elements here, independent of the chemi-
cal compound or mineral which contains these elements, and among the
elements themselves, to those which are present in a non-gaseous state
in the ice, and which are thus found in the state of particles sus-
pended in the atmosphere prior to being deposited on the envisaged
glacier. It is not that the nature of chemical compounds or mineral
and organic particles, or that the nature of gas have nothing of interest
to offer (numerous reports presented here elequently contradict such
a premise), but rather it is simply because one must limit oneself,
and because the elementary composition is often the best known para-
meter, the best established parameter from the statistical viewpoint,
and because it represents an initial level for chemical research.

'79/   From a genetic point of view, four principal sources can be dis-
cerned, which furnish the impurities in the ice. The specific contri-
butions from these sources have a composition and relative volume
that vary considerably in space and time. We will denote the fol-
lowing sources, symbolizing them as follows:

    oceanic: O
    crustal: C
    extraterrestrial: E
    human or anthropogenic: H

In its most general form, the problem is presented as follows:
let $\underline{/E_1\underline{/}}$, $\underline{/E_2\underline{/}}$, ..., $\underline{/E_i\underline{/}}$ be the concentrations measured in the
ice of i elements E_1, ... E_i. One can write i equations which simply
express that the total quantity of element E_i is equal to the sum of
the quantities of this element coming from each of the sources:

$$[E_i] = [E_i]_O + [E_i]_C + [E_i]_\varepsilon + [E_i]_{ii}$$

$$\vdots$$

$$[E_i] = [E_i]_O + [E_i]_C + [E_i]_\varepsilon + [E_i]_{ii}$$

It is then a question of determining from the i concentrations measured, all the terms which are given by the members of the right-hand side of the equation i.e., to determine simultaneously the contribution of each of the sources to each element, as well as the chemical contribution of the four contributions.

We will note that the problem rarely presents in such a general form; more often, one of the following particular cases exists:

(1) To evaluate the percentage of the composition from one of the sources. Example: to evaluate the percentage of extraterrestrial material on the globe from the Ni content of polar snow.

(2) To evaluate the relative contribution of one of the sources with respect to a certain element present in the ice. Example: to evaluate the contribution of Pb found in a glacier due to man's activities.

(3) To evaluate the chemical composition of one of the deposits. Example: to determine the composition of the oceanic contribution in view of establishing whether this deposit differs or does not differ from the composition of sea water.

The general problem is presented in the form of a system of i linear equations for $4 \times i$ unknowns; its solution is indeterminate.

The ruse commonly employed to eliminate the indeterminate nature

consists in introducing, by way of supplementary equations, the

concentration ratios of two elements coming from the same source,

or those of the same element in two contributions, coming from two

separate sources.

In the first case, $(i - 1)$ ratios relative to a given source are

used. For example, for an oceanic source, one could write:

$$\frac{[E_2]_0}{[E_1]_0} = R_{2:0}; \qquad \frac{[E_3]_0}{[E_1]_0} = R_{3:0}; \ldots; \qquad \frac{[E_i]_0}{[E_1]_0} = R_{i:0}$$

The four sources will furnish $4(i - 1)$ supplementary relations

which, when added to the preceeding i equations, permit the writing

of $(5i - 4)$ equations for $4i$ variables. The system would become

determinate as soon as the concentrations of at least four elements

are known, and additionally as soon as the R ratios of the concentra-

tions in the <u>contributions</u> are known.

/80/   However, the chemical composition of contributions is <u>a priori</u>

unknown, so that one is indeed caught up in a vicious circle. In

order to solve this problem, one often ends up identifying the R con-

centration ratio of two elements in the contribution from a given source

with the average geochemical ratio of these two elements in this same

source. It is current practice to make the following assignments:

    (1) oceanic contribution - composition of sea water;

    (2) crustal contribution - average composition of the terrestrial
        crust;

    (3) extraterrestrial contribution - the average composition of
        chondritic meteorites.

Used without question, this process is obviously fallacious, because we know that intense chemical fractionations can occur at every phrase of production, transport, and deposit of particles from the atmospheric aerosol. In addition, since the quantities injected into the atmosphere are absolutely minimal with respect to the volume of these sources, one cannot argue for the necessity of maintaining a state of stationary equilibrium in the chemical composition of the various sources, in order to derive from them any restrictive supplementary conditions.

Upon first glance, the oceanic source seems to pose the fewest problems; is not the ocean composition in fact well known and practically constant in space and in time, just the opposite of the situation for the other sources? In reality, indicators accumulate in favor of the idea that, as soon as they leave the surface of the water, particles of oceanic origin, or at least the smallest fraction, which will fall very far away, have a composition very different from that of sea water. It would appear that the true source of sea aerosols is found at the level of the first millimeter, or even the first few microns, from the surface, and that the composition of this microlayer is doubtlessly very different from that of sea water; in addition, this layer varies greatly in time and in space.

The crustal source is understood here as the non-oceanic natural terrestrial source. To assign this average crustal terrestrial composition to a crustal contribution seems ludicrously simplistic.

The crustal contribution to the atmospheric aerosol in fact comes from two partial and very different sources:

(1) doubtlessly the most important, the lithosphere-atmosphere interface, or, more simply, the soil, which is the arena for very complex biological and physicochemical processes; and

(2) the other, which is comprised of the deeper layers of the lithosphere or even of the upper mantle, which come into contact with the atmosphere by means of volcanos.

It is of no use to insist on the importance of chemical fractionation which come into play in this case. It is sufficient, for example, to compare the composition of volcanic smokeholes with that of the lava which produced them.

There is particular interest in identifying the volcanic contribution. In ice core samples from polar caps in Greenland or Antarctica, such an identification, associated with $\delta(^{18}O)$ or $\delta(D)$ isotopic ratio profiles, would permit looking at the global volcanic activity under climatic conditions, and to derive from this comparison convincing arguments in favor of or against the hypothesis that volcanic activity is a determining factor in climate.

The _extraterrestrial source_: the contribution from this source is minimal in volume, but it is of great interest, due to astrophysical and geochemical implications. Meteorites constitute the

/81/ most spectular form of extraterrestrial contribution, but we are led to believe that extraterrestrial material is brought to us principally in the form of a continuous rain of microscopic dust,

whose presence in interplanetary space is attested to by various

phenomena: zodiacal light, meteors, impacts on detectors mounted

on board space probes.

Here also, one must subdivide the extraterrestrial contribution

into two partial contributions: meteoritic, with a well known composi-

tion, but whose total amount is minor, and an interplanetary-dust

contribution, predominant by volume, but whose composition is

practically unknown.

The human source: here, the following distinction must be made:

(1) industrial wastes in the atmosphere, i.e., local and

global pollution; and

(2) the contribution resulting from manipulations in collect-

ing, treating, and analyzing the samples, or in other words, contamina-

tion.

This distinction is of manifest methodological interest. In the

case of polar snows, in particular, where impurities are measured in

ppb and fractions of ppb, the risks of contamination are enormous, and

the determination of the contamination factor constitutes an essen-

tial condition of the validity of results. Modern analytical methods

permit us to detect almost any element at any concentration level;

the real problem at such concentration levels is not to detect some-

thing that has been introduced into the sample.

We will note also, still with respect to polar snows, that

recourse to deep beds deposited before the explosive expansion of

industrial activity may reduce to zero the pollution contribution,
but will never reduce contamination risks; in fact, the contrary is
true.

It would therefore be desirable, in view of objectives commonly
pursued, to refine the table of sources, at least by introducing the
following distinctions:

O = ocean + surface microlayer.

C = soils + volcanos.

E = products of meteoritic ablation + interplanetary dust.

H = pollution + contamination.

These distinctions, by doubling the number of unknowns, obvious-
ly do not at all facilitate the problem of identification of sources,
given our ignorance of the composition of the contributions.

In conclusion, one would be tempted to conclude from the preced-
ing that there is no element that can furnish by its presence or absence
alone unequivocal proof of its origin, and that the content of such
and such an element will teach us nothing quantitative with respect
to the relative contribution of the various sources given above.

Even if this conclusion is ultimately true, we may temper our pes-
simism with the observation that it is nevertheless possible to find
important indications, although these are essentially qualitative, of
the elementary composition itself. It is, in fact, legitimate to give
to each of these sources one or more "indicator" elements, whose
relative content in the source in question is so different from that
present in the other sources, that it should characterize the respective

contribution, however many intervening chemical fractionations.

This is obviously the case, for example:

of Cl (or if this is lacking, of Na) for the oceanic contribution;

of Si, of Al, of Ti, etc. for the continental contribution;

/82/ of siderophilic elements, such as: Ni, Os, Ir, Pt, for the meteoritic contribution; and

of certain exotic elements, typical of industrial activity, for the pollution contribution.

As far as the contamination contribution is concerned, although it is always undesirable, the coherence and reproducibility of results will prove nothing in this regard; they can simply reflect constant levels of systematic contamination. Only judiciously designed blank tests will be able to prove the absence of systematic contamination. And even satisfactory blank tests do not exclude the possibility that accidental contaminations will affect certain measurements, a fact that is often annoying, because they involve unexpected or exceptional results which are in principle the most worthy of interest.

Be that as it may, it is difficult, it seems to me, to escape the conclusion that chemical arguments in themselves are not sufficient, and have not been sufficient up to now to provide irrefutable proof on the origin of a given element present in ice, to evaluate with precision the contribution of one of the sources, or even to define the exact composition of one of these contributory sources. Chemical arguments should be supported by supplementary data, but of what nature?

Much is expected of the examination of individual particles. The optical microscope has without doubt been employed to its limit , but the use of the transmission electron microscope combined with electron diffraction, and, more recently, recourse to the scanning electron microscope combined with microprobe x-ray spectroscopy, or even the introduction of the ion microscope combined with mass spectrometry, open up very promising prospectives, and have already furnished results of very great interest. Several reports presented at this symposium have provided remarkable examples.

In order to remain within the framework of the present study, and with respect to extending chemical methods, I would call for the possibility of complementing purely chemical attempts at identifying sources with certain nuclide determinations, either radioactive or stable. In certain favorable cases, unfortunately rare, one can define with no ambiguity the origin of chemical elements to which these nuclides belong, or from which they originate. By way of example, I will discuss very briefly the results of two studies that have been made within the framework of a collaboration between various departments and institutions, including the Free University of Brussels.

The first case illustrates the employment of a natural radioisotope, ^{53}Mn, in order to demonstrate the extraterrestrial origin of Fe present Antarctic snows. In the second case, use is made of the ratios for the abundance of stable isotopes of Pb in order to prove and define the anthropogenic origin of a portion of Pb present in an Alpine glacier.

EVALUATION OF THE CONTRIBUTION OF EXTRATERRESTRIAL MATERIAL FROM CONCENTRATIONS OF Ni AND [53]Mn MEASURED IN THE FIRN AT THE PLATEAU STATION (EAST ANTARCTIC PLATEAU)

This study was the result of a large international collaboration.

The intervention of the US Antarctic Research Program and the National Science Foundation of the USA permitted sampling several tons of firn at the Plateau Station and to transport them in a solid state to Brussels.

Chemical analyses were based on the use of the BR1 reactor of the Belguim Nuclear Energy Research Center at Mol. Finally, the measurement of [53]Mn, the details of which have been published by Bibron et al. (1974) were carried out at the CNRS-CEA Combined Laboratory - Center of Weak Radio Activity at Gif-sur-Yvette (France), directed by J. Labeyrie and with the collaboration of the reactor team EL3 of the CEA at Saclay (France).

/83/

In a first step, purely chemical, the presumed concentration of extraterrestrial material was deduced from measured contents of Fe and Ni. This result, certainly interesting with respect to the limits it imposes on a large number of astrophysical and geochemical parameters, however, is highly suspect with regard to accuracy, due to the numerous little-supported hypotheses on which it is based.

A second step, based on the determination of [53]Mn in the same firn layers has permitted a confirmation of validity by demonstrating without ambiguity the extraterrestrial origin of a part of the Fe found.

The geographical and climatic characteristics of the Plateau Station ($79°$ 15' S, $40°30'$ E, altitude 3700 m, mean annual temperature of

12.

−60°C) and the possibilities of access offered at the time sufficed
to justify the choice of sampling site.

The choice of Ni as an indicator element of the extraterrestrial
contribution is evidently based on the hypothesis, explained below,
that since this contribution has a chondritic composition, it lends
itself also to experimental measurement possibilities.

The choice of ^{53}Mn (radioactive nuclei disintegrating via elec-
tron capture with a half-life of approx. 2×10^6 years) as an unequivocal
indicator of extraterrestrial origin is based on the fact, that has
been well established since the first theoretical studies made by
Wasson (1963) and later by Lal and Venkatavaradan (1967), that this
nuclide can be formed only in extraterrestrial space, principally by
interaction between solar cosmic radiation and the Fe contained in
microscopic dust which has sojourned in interplanetary space for
several tens of thousands of years.

The steps taken can be schematised as follows, using the nota-
tions defined above; one can write:

$$[Ni] = [Ni]_0 + [Ni]_C + [Ni]_E + [Ni]_H$$
$$[Fe] = [Fe]_0 + [Fe]_C + [Fe]_E + [Fe]_H$$

From analyses conducted on about twenty specimens of approx. 2 kg,
it resulted that the average concentrations of Fe and Ni in the firn
deposited during the approximate period 1950-1955 are:

$/Ni/$ = 0.03 ppb
$/Fe/$ = 2.8 ppb

The error margins are omitted, because it would take too long to ex-
plain their significance.

Let us instead say that the Ni was measured by neutron activation of the specimen maintained in the solid state and irradiated in the lucite container which was used for sampling. This method is the surest method, if not the only method, for success on the scale of hundredths of ppb, because it permits a simultaneous control of losses (by the harmless of addition of a stable isotopic carrier after irradiation) and contamination (by a significant blank test covering every stage of the sampling and of the analysis); unfortunately, it involves considerable technical difficulty at the irradiation level, and it can be applied only to a limited number of elements, not including Fe.

Fe was measured by atomic absorption after concentrating the sample; the result found is somewhat more uncertain. A detailed description of the experimental procedures is recorded in the theses of Vosters (1970) and Hanappe (1970).

The following hypotheses are introduced by way of supplementary equations:

(1) The oceanic contribution of Ni and Fe is null:

$$\underline{/Ni/}_0 = \underline{/Fe/}_0 = 0$$

This hypotheses is based on the measured concentrations of Na and K (approx. 30 ppb and 2 ppb, respectively).

(2) The crustal contribution has a composition analogous to the "mean terrestrial crustal composition", which involves the following equation:

$$\underline{/Fe/}_C / \underline{/Ni/}_C = 750$$

/84/

It should be recalled that this ratio is approx. 60 in basaltic rock and 50,000 in granite.

(3) The extraterrestrial contribution has a composition analogous to that of carbonaceous chondrites, which involves the following equation:

$$[Fe]_E / [Ni]_E = 19$$

and the extraterrestrial material concentration $[A]_E$ is such that:

$$[Ni]_E = 0.012 \times [A]_E.$$

(4) The anthropogenic contribution (pollution plus contamination) is null:

$$[Ni]_H = [Fe]_H = 0.$$

The plausibility of a zero pollution is based on the geographical characteristics of the sampling site and on the fact that the samples were taken from layers deposited prior to 1952.

The plausibility of a zero contamination is based on the quality of the blank tests; this quality is very high for Ni, but less so for Fe.

From this system of equations, one finds that:

$$[Ni]_E = 0.023 \text{ ppb}$$
$$[Fe]_E = 0.43 \text{ ppb};$$

therefore, 85% of the Ni and 15% of the Fe were of extraterrestrial origin.

As far as the ^{53}Mn is concerned, measurement produced a specific activity equal to (0.8 ± 0.2) dpm. The very detection of this nuclide surprisingly and surely demonstrates the presence of Fe of

extraterrestrial origin in these specimens. Starting with the activity detected and with a certain number of theoretical and experimental data, one can show that the content of extraterrestrial Fe should be found within the extreme limits of 0.5 ppb and 5 ppb. Despite the wide margin of uncertainty, this conclusion agrees with that deduced from chemical results, giving it very serious support. It also supports hypotheses relating to these chemical results, thus elevating them from the plane of the plausible to that of the very highly probable. A detailed report of the various repercussions that this result has for properties of interplanetary dust is found in the above-mentioned publication by Bibron et al. (1974).

ISOTOPIC COMPOSITION AND ORIGIN OF Pb FOUND IN AN ALPINE GLACIER

This study was carried out within the framework of an association agreement between the Free University of Brussels and the European /85/ Economic Communities. It was conducted with the collaboration of Mr. Paul Pasteels of the Free University of Brussels (Belgium) in conjunction with the Geochemical Laboratory of the University of Paris VII (France), directed by Mr. Claude Allegre. The results presented here are from Miss I. Cousin and Messrs. G. Manes, D. Petit, and R. Souchez, who have willingly reported them prior to publication.

We shall recall first that the abundance of stable isotopes (or primary radioactive isotopes) which comprise a poly-isotopic element is generally constant; it shows no detectable variation as a function of the origin of this element that can be found with the most sensi-

tive methods available to date (i.e., no relative variation greater than approx. 10^{-4}), with the <u>exception</u> of two classes of elements:

(1) <u>Light elements</u>, particularly hydrogen, oxygen, carbon, and sulfur, which enter into the composition of molecules capable of undergoing isotopic fractionations, generally small but measurable, during various physico-chemical processes to which they are subject in nature.

(2) <u>Heavier elements, which have one or more radiogenic isotopes</u>, i.e. resulting from the disintegration of a radioactive parent nuclide. In this case, the abundance of the radiogenic isotope can vary within very broad limits as a function of various factors that are impossible to dwell on in detail here. These variations are particularly high and relatively well understood in the case of two elements: Pb and Sr.

Pb includes four stable isotopes, one of which, ^{204}Pb, is not radiogenic, while ^{206}Pb, ^{207}Pb, and ^{208}Pb are capable of forming from the radioactive disintegration of ^{238}U, ^{235}U, and ^{232}Th, respectively. It follows that the isotopic composition of Pb of an ore varies appreciably from one bed to another, as a function of various factors, particularly the age of the bed and the geochemical ratios of Pb/U and Pb/Th in the mother rock which gave rise to the bed. One can state very schematically that the older the bed, the poorer the radiogenic isotopes of Pb: ^{206}Pb, ^{207}Pb, and ^{208}Pb, with respect to ^{204}Pb.

Since the first measurements were made by Murozumi et al. (1969) on Greenland ice, numerous observations have confirmed that the concentration of Pb in various media capable of reflecting and storing the atmospheric composition (glaciers, sediments, etc.) has considerably increased during the last few decades. This increase has been attributed to the increasing consumption of automobile gasoline, which contains alkylated Pb compounds used as anti-knock agents.

In the course of a study on atmospheric pollution by Pb in Europe, an attempt was made to trace the evoluation of the Pb content in the atmosphere by depositing this element in certain amounts in various media, particularly in specimens of an Alpine glacier (the Tsanfleuron glacier in the Vaudoises Alps, Switzerland). The first analyses conducted on two extreme samples, one of which was very recent, and the other of which was more than 50 years old, showed the following Pb contents:

    recent snows = 1.4 ppb
    old ice = 0.33 ppb

Although these results are not as easy to interpret as in the case of polar glaciers, due to the risks of percolation and mixing, they indicate that the Pb content has approximately quadrupled during the last 50 or so years.

/86/   In order to confirm the origin of this increase in Pb, the analysis of stable isotopes was made. In fact, observations show that in spite of the great variations in space and time, the Pb contained in gasoline is, on an average and in our area, relatively less

radiogenic (poorer in the isotopes ^{206}Pb, ^{207}Pb, and ^{208}Pb) than the Pb associated with industrial wastes or than the actual average Pb of the terrestrial crust, which should correspond on an average to the Pb present in natural atmospheric dust.

The reason for this state of affairs is essentially of an economic and commercial nature: Alkylated Pb is fabricated by a small number of companies, whose supply of Pb is assured for the most part by Precambrian beds.

The results obtained are summarized in Fig. 1. The Pb of present snows is less radiogenic than Pb of old ice. Its isotopic composition conforms on an average to that of the Pb contained in Swiss gasoline, measured by Chow, personal communication, 1970). It would be premature to calculate a balance sheet from such a small number of data, but isotopic measurements demonstrate unambiguously, the presence of a large anthropogenic contribution resulting from automobile gasoline consumption.

By way of conclusion, one might ask oneself if this approach can be extended to other sources, using other elements, light or heavy, depending on the case. The outlook in this respect, although it is not negligible, is not particularly encouraging. Without discussing technical difficulties associated with the separation and analysis of elements present in very minute traces in ice, the distinction between oceanic and crustal source by means of stable /87/ isotopes encounters a serious difficulty of principle: the elements,
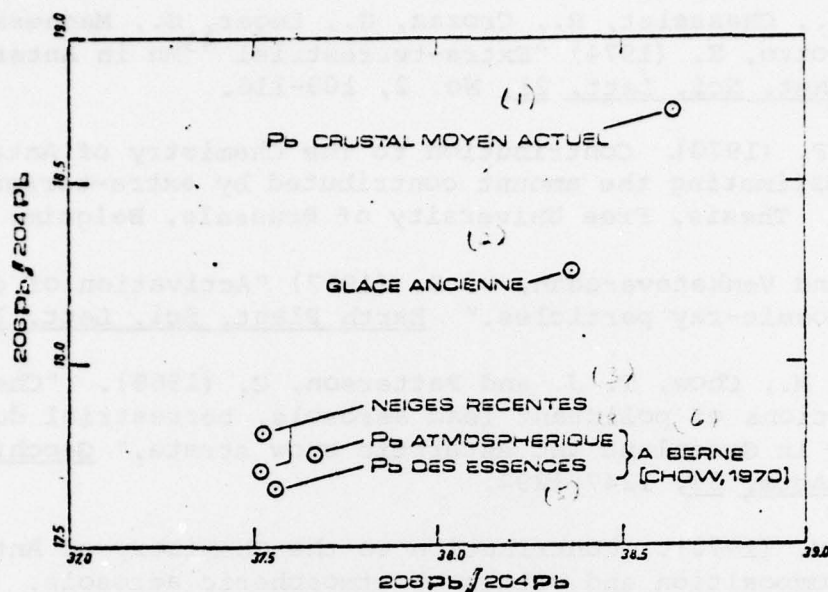
Fig. 1. Isotopic ratios of Pb from samples taken from the Tsanfleuron
glacier (Vaudoises Alps, Switzerland); the Pb of current
snows is less radiogenic than the Pb of old ice. Its iso-
topic composition conforms to that of Pb contained in Swiss
gasoline (Chow, personal communication, 1970).

Key: (1) Current average crustal Pb;   (2) Old ice;   (3)   Recent snow;

(4) Atmospheric Pb;   (5) Gasoline Pb; (6) At Berne (Chow, 1970).

particularly Sr and Pb, contained in the ocean are essentially of a

crustal origin (erosion of continents and terrestrial or undersea

volcanos). They have an isotopic composition that corresponds to the

average crustal composition.   Upon first glance, one would not

expect to find appreciable differences in the isotopic composition of

these two sources. This is, however, not a valid motive for not

pursuing research in this direction.

REFERENCES

1. Bibron, R., Chesselet, R., Crozaz, G., Leger, G., Mannessier, J. P. and Picciotto, E. (1974) "Extra-terrestrial [53]Mn in Antarctic ice." *Earth Planet. Sci. Lett.* *21*, No. 2, 109-116.

2. Hanappe, F. (1970). Contribution to The Chemistry of Antarctic Snows. Estimating the amount contributed by extra-terrestrial material. Thesis, Free University of Brussels, Belguim.

3. Lal, D. and Venkatavaradan, V. S. (1967) "Activation of cosmic dust by cosmic-ray particles." *Earth Plant. Sci. Lett.* *3*, 299-310.

4. Murozumi, M., Chow, T. J. and Patterson, C. (1969). "Chemical concentrations of pollutant lead aerosols, terrestrial dusts and sea salts in Greenland and Antarctic snow strata," *Geochim. Cosmoch. Acta.* *33*, 1247-1294.

5. Vosters, M. (1970). Contribution to the Chemistry of Antarctic snows. Composition and origin of atmospheric aerosols. Thesis, Free University of Brussels.

6. Wasson, J. T. (1963, "Radioactivity in interplanetary dust". *Icarus* *2*, 54.

DISCUSSION

Lorius:

I think that your very interesting report rather greatly diminishes the pessimistic attitude under which you presented the problem of qualitative and quantitative identification of the sources in your introduction. It seems to me to show that it is necessary to develop not only methods of identification based on isotopic determinations, but also those using concentration ratios, or the examinations of individual particles.

Picciotto:

I agree. However, chemistry alone cannot give us results which are completely clear. These results should be confirmed by oceanic and continental data, which is the major problem.

de Quervain:

When you quoted the figure of 80 000 t/year of total influx of cosmic matter, I asked myself, how you did obtain it. Is this an average value, and if so, how did you obtain this average?

Picciotto:

It is an average value, but it would take considerable time to explain how it was obtained. It was derived from stratospheric fallout data, using certain factors to compensate for stratospheric fallout being not uniform.